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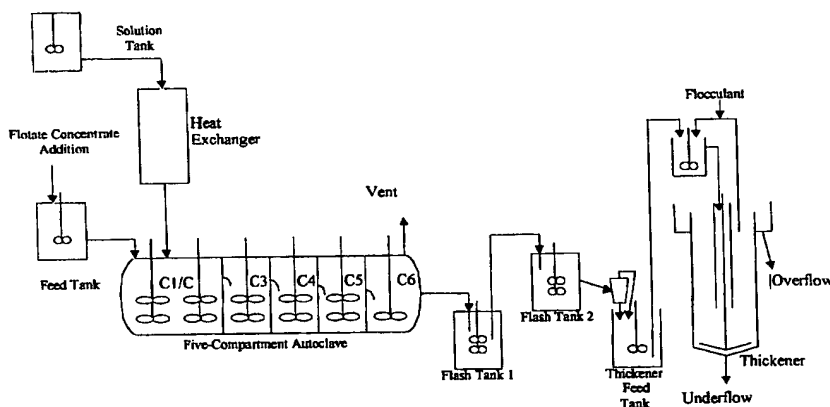
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FLOW CHART FOR CONTINUOUS TEST RUN FOR 60 HOURS
WITH SHIFT OPERATING DUTY

(57) Abstract: This invention addresses the elimination of both organic and inorganic total carbon resulting from carbonates and organic matters contained in zinc silicate concentrates. As it takes full advantage of the neutralizing power of the floated concentrate, this process has two additional benefits: its high efficiency in removing magnesium, an element that is detrimental to the electrolytic process in zinc production, and its capacity of fully purging the excess waters in the hydrometallurgical zinc process which causes dilution in the metal production circuit. This process consists of the direct high-pressure treatment of the zinc silicate concentrate in autoclaves at elevated temperature with secondary Zn-bearing solutions, thereby avoiding the costly calcination (600-900°C) or calcine grinding stages, as the granulometry that is obtained from the concentrate flotation and enrichment process is enough for reactions at high temperatures and pressures.

WO 2004/020678 A1

A PROCESS TO ELIMINATE BOTH ORGANIC AND INORGANIC TOTAL CARBON IN ZINC SILICATE CONCENTRATE, WITH AN ADDITIONAL EFFECT OF PURGING BOTH WATERS AND MAGNESIUM IN THE ZINC PRODUCTION CIRCUIT.

5 This invention is designed to provide an innovative process to totally remove organic matters and carbonates from zinc silicate concentrates, as well to purge water and magnesium at zinc plants.

Organic matters are detrimental to the zinc production process, especially at the purification stage as well as at the electrolytic process, as they reduce metal
10 electroplating efficiency and cause sticky to the cathodic deposit, thus adversely affecting stripping at the cathodic plate. With the conventional process organic matters are removed by way of a costly concentrate calcination process at high temperatures exceeding 600°C.

Since the water balance must be fine adjusted in the zinc production process, this balance adjustment often requires sacrificial cells in the zinc electrolysis and low zinc exhaustion contents for the subsequent zinc precipitation stages with lime or limestone addition for the effluent treatment, or by simple neutralization, thus leading to metal recovery losses. This invention uses at a maximum the neutralization power of the very zinc concentrate and takes advantage of the proper
20 conditions for maximization of reaction kinetics with high metal recovery efficiencies.

Magnesium is another element harmful to a zinc production process. This element not only adversely affects the impurity removal stage but also cause the ohm resistance of the zinc electrolytic bath, thus decreasing electroplating efficiency. This
25 invention provides the necessary selectivity in order to leave the element magnesium

in solution for total purge of the liquid phase and extraction of most part of this element found in the treated concentrate.

Therefore, the chief advantages of this new process are:

- totally eliminates flotated concentrate calcination (600-900°C) ;
 - eliminates subsequent grinding of the resulting calcine;
 - reduces the zinc content in effluents for the necessary neutralization;
 - eliminates foams during the flotated cake leaching stage;
 - increases the zinc electroplating efficiency by obtaining an organic matter free solution;
- 10 • increases the overall zinc recovery output by dramatically reducing metal neutralizations and recycling operations whose processes often result from ineffective neutralizations.

In order to meet these purposes the Applicant has developed a total organic and inorganic carbon and magnesium elimination process in zinc silicate flotated concentrate with an added effect of purging waters in the zinc production circuit

15 characterized by the direct treatment of the autoclave-flotated concentrate, at high pressure and temperature, with secondary solutions containing zinc.

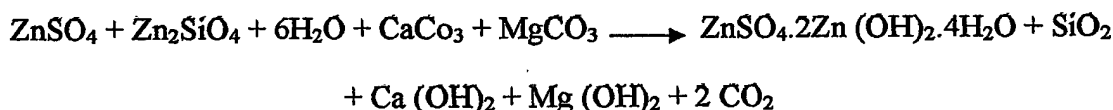
This process consists of treating the zinc silicate flotated concentrate, with no calcination, with secondary or wash zinc solutions in autoclaves at temperatures

20 ranging from about 160°C to about 200°C and pressures from 11 bar to 19 bar. The determination of the working temperature/pressure conditions on the autoclaves depends upon the

residence time available on the autoclaves. The longer the residence time, the lower the required temperatures and pressures to meet the objectives, namely: total carbon

decomposition in the form of carbonates and/or in the form of organic matters; selective zinc precipitation and magnesium extraction for the liquid part. Following autoclaving, the pulp may be discharged to flash tanks in order to reduce both pressures and temperatures up to atmospheric condition. The resulting pulp is thickened and filtered. The low zinc content filtrate may be directed to either the neutralization or effluent treatment section, and the cake may be leached using sulphuric acid to produce zinc sulphate solution.

Within the autoclaves the initial pressure is produced by the added vapor, but subsequently it rises with the decomposition of the carbonates and organic carbon, which are converted into carbon gas and water as shown from this reaction:



Since the selective zinc precipitation from secondary solutions generates a high output with the benefit of the reaction kinetics at high temperatures and pressures, which are not possible with conventional reactors, the plant effluent treatment system using this technologic innovation will have a decreased contribution of the metal to treat, thus promoting productivity and cutting down on the consumed reagents.

The leaching stages of the autoclave-treated flotated concentrate presented excellent zinc recovery outputs (98.5%), with the additional advantage of improved times for filtration and thickening of the leached pulp for leaching of the autoclave-treated flotated concentrate versus the conventional calcine leaching process.

The overall zinc recovery output on silicate plants is increased with this new process because the inefficiencies of metal recycling under the effluent treatment are not present.

The following are illustrative examples which should not be considered as limiting the invention's scope.

In order to test this process bench-scale experiments have been ordered using amounts of raw flotated concentrate ranging from 100g to 2000g, as well as
5 continuous duty tests run on a pilot plant for 200Kg/day operating 24 hours a day during 60 hours.

EXAMPLE 1:

BENCH-SCALE TESTING RUN IN LABORATORY:

The first tests were conducted in laboratory within April 8 and April 11,
10 2002.

The autoclave treatment testing of the raw flotated concentrate was bench-conducted using 100 g sample, 160°C temperature, and synthetic solution to simulate the secondary with 39 g/L Zn and 4 g/L Mg. The residence time was set to 90 minutes. Following the autoclave treatment testing of the raw flotated concentrate,
15 the liquid was discarded and the resulting cake was added to a sulphuric acid solution at 200 g/L to simulate the starting leaching and check for foam formation.

The results of the autoclave treatment of the raw concentrate using zinc sulphate synthetic solution and magnesium are shown in Figure I attached herewith.

The cakes resulting from filtration of the autoclave treated concentrate were
20 added to a sulphuric acid solution at 200 g/L to simulate silicate concentrate leaching conditions; the qualitative results are shown in Figure II attached herewith.

TEST CONCLUSIONS:

- The zinc contained in the secondary synthetic solution was precipitated with excellent performance in the autoclave;
- 25 • No magnesium precipitation occurred, but in contrast about 60% of element in

the concentrate was extracted;

- The zinc precipitation efficiency was as high as 99% (test 4);
- The treatment of the raw concentrate eliminated the carbonate from the concentrate, as evidenced by the appearance of no effervescence during leaching,
5 but no carbonate or total organic matter analyses have been conducted with the leached filtrate;
- No foam formation occurred during leaching, an evidence of decomposition of the organic matter and carbonates converted into CO₂ and water, which is demonstrated by the increased autoclave pressure;
- 10 • Because of the successful tests with the autoclave treatment of the raw willemite concentrate, a second testing stage was suggested to confirm the results using larger scale tests.

EXAMPLE 2:

CONFIRMATION OF THE RESULTS OF THE RAW
15 CONCENTRATE TREATMENT WITH LABORATORY BATCH
TESTING:

The tests were conducted within April 22 and April 25, 2002.

The composition of the concentrate used for the autoclave tests was as follows:

20 Chemical Analysis:

Zn (%)	MgO (%)	CaO (%)	F (%)	Carbonates (%)	SiO ₂ (%)	Moisture (%)
42.74	2.32	3.22	0.0210	8.72	27.0	8.6

Granulometry:

Sieve (mesh)	60	80	100	170	200	270	325
Unders (%)	99.8	98.7	95.5	81.4	75.4	68.6	63.2

TEST 1 - Determining the optimal autoclave operation time:

The secondary solution was synthesized from the composition of the solution with initial analysis as follows:

Solution analysis	G/ L
Ca	0.12
Mg	3.79
Mn	0.68
Si	0.25
Zn	31.7
PH	4.00

5

The autoclave feed pulp was prepared using the zinc silicate flotated concentrate and synthetic secondary solution at 20% solids.

The autoclave-treated test of the flotated concentrate monitored the results every 30 minutes of reactions in order to determine the best residence time. The operation parameters used as well as the test results are shown in Figure III attached herewith.

TEST 2 -- Limestone addition (calcium carbonate) to improve efficiency of the neutralization and precipitation of the zinc contained in the secondary solution:

Both test conditions and results are shown in Figure IV attached herewith.

As can be seen from the results, there is evidence that the zinc precipitation efficiency rose to 99.9%. No magnesium precipitation occurred but rather it

solubilized in the concentrate at around 60%, an evidence of how powerful the zinc production process is in removing this harmful element.

The leaching was tested of the cake obtained under this test number 2, and the result thereof demonstrated no foam formation. The TOC - Total Organic Carbon - analysis confirmed that no organic carbon was present, and a chemical analysis thereof showed a content lower than the detection range of the analysis apparatus, i.e., 4 mg/liter, as indicated in Figure V attached herewith.

CONCLUSIONS:

- Proof of zinc precipitation efficiency and magnesium extraction was evidenced by batch tests using larger amounts of fed materials.
- The organic matter is decomposed in the autoclave into CO₂ and water, which was practically demonstrated not only by the elimination of effervescence and foaming but also by TOC - Total Organic Matter - chemical analysis, matter which was not detectable when the autoclave-treated cake was leached. Under the raw concentrate leaching test, with no treatment, this was 80 ppm.

EXAMPLE 3:

CONTINUAL TREATMENT TESTING OF FLOTATED CONCENTRATE, WITH NO CALCINATION, IN PILOT PLANT USING LABORATORY AUTOCLAVES:

Continuous treatment tests were conducted of the raw flotated concentrate with the purpose of reproducing results which had already been reached with batch tests within June 12 and June 17, 2002.

Continual Test Flow Chart – this is shown in Figure VI attached herewith.

The results are found in Figures VII through IX attached herewith.

Test time was 60 hours, using continuous duty with rotation shift. The results

demonstrated that:

- The zinc precipitation and magnesium efficiencies were best with 25% solid concentration.
- The optimal residence time was 90 minutes at 200°C, which resulted in leached autoclave-treated cakes WITH NO FOAM FORMATION.

EXAMPLE 4:

LEACHING TEST OF CAKES RESULTING FROM THICKENER UNDERFLOW FILTRATION IN LABORATORY:

This consisted of continuous pilot tests designed to determine leaching performance of autoclave cakes considering the following: foam evolution, filtration time, sedimentation, and leaching output.

The tests used autoclaved concentrates and leaching solution with 196 g/l acidity, 65 - 70°C temperature, and 07:00 h residence time.

The results are shown in Figures X through XII attached herewith and are as follows:

- Mg concentration is reduced by 1 g/l in the solution resulting from the leaching using the autoclaved concentrate;
- Leaching outputs were very good: approximately 98.5% of zinc extraction;
- Fluoride content decreased by 7 mg/L (see Figure XIV attached herewith);
- Thickening and filtration efficiencies were better in the leaching of the autoclave-treated flotated concentrate than the leaching of silicate calcines, which permits a reduction in the size of such items of equipment as thickeners and also in the filtration area;
- The tests evidenced that no foam formation occurred during leaching of the autoclaved concentrate.

- Figure XIII attached herewith shows comparative sedimentation efficiencies in 250 ml test tube (at 33% dilution) for the autoclave-treated flotated concentrate.

CLAIMS

1. A process to eliminate both organic and inorganic total carbon in zinc silicate concentrate, with an additional effect of purging both waters and magnesium in the zinc production circuit, characterized by the direct treatment of the autoclave-
5 floated concentrate, at high pressure and temperature, with secondary solutions containing zinc.

2. A process to eliminate both organic and inorganic total carbon in zinc silicate concentrate, with an additional effect of purging both waters and magnesium in the zinc production circuit according to claim 1, characterized by the fact that,
10 following autoclaving, the pulp may be discharged into flash tanks, in order to reduce both pressure and temperature up to atmospheric condition.

3. A process to eliminate both organic and inorganic total carbon in zinc silicate concentrate, with an additional effect of purging both waters and magnesium in the zinc production circuit according to claims 1 and 3, characterized by the fact
15 that the pulp obtained may be thickened and filtered.

4. A process to eliminate both organic and inorganic total carbon in zinc silicate concentrate, with an additional effect of purging both waters and magnesium in the zinc production circuit according to claim 1 characterized by the fact that the low zinc content filtrate may be directed to either the neutralization or effluent
20 treatment section and the cake may be leached using sulphuric acid to produce zinc sulphate solution.

5. A process to eliminate both organic and inorganic total carbon in zinc silicate concentrate, with an additional effect of purging both waters and magnesium in the zinc production circuit, characterized by the fact that the zinc silicate floated
25 concentrate may be treated, with no calcination, with secondary zinc

solutions in autoclaves at temperatures ranging from about 160°C to about 200°C e pressures from 11 bar to 19 bar.

6. A process to eliminate both organic and inorganic total carbon in zinc silicate concentrate, with an additional effect of purging both waters and magnesium
5 in the zinc production circuit according to claim 5, characterized by the fact that, following autoclaving, the pulp may be discharged into flash tanks, in order to reduce both pressure and temperature up to atmospheric condition.

7. A process to eliminate both organic and inorganic total carbon in zinc silicate concentrate, with an additional effect of purging both waters and magnesium
10 in the zinc production circuit according to claims 5 and 6, characterized by the fact that the pulp obtained may be thickened and filtered.

8. A process to eliminate both organic and inorganic total carbon in zinc silicate concentrate, with an additional effect of purging both waters and magnesium in the zinc production circuit according to claim 5, characterized by the fact that the
15 low zinc content filtrate may be directed to either the neutralization or effluent treatment section and the cake may be leached using sulphuric acid to produce zinc sulphate solution.

FIGURE I**RESULTS OF BATCH TESTS USING 100G OF FLOTATED CONCENTRATE
WITH NO CALCINATION**

Number	Pulp Solution Contents		Solid Percent	Filtrate Contents Following Autoclave Treatment		Zn and Mg Efficiencies	
	Zn (g/L)	Mg (g/L)		Zn (g/L)	Mg (g/L)	Zn (%)	Mg (%)
01	39	4	20	8	6	80	170
02	39	4	25	2,3	7	92	170
03	39	4	30	0,9	7	96	170
04	39	4	25	0.7	7	99	170

Three grams of sodium carbonate were added for test 4 in order to extract fluorides from the concentrate.

FIGURE II**RESULTS OF QUALITATIVE TESTS DESIGNED TO CHECK FOR
FOAM FORMATION AND / OR EFFERVESCENCE**

Number	Quantity of acid solution in ml	Quantity of cake from autoclave in g	Visual check of foam formation
01	200	100 – test 1	No foam or effervescence
02	200	100 – test 2	No foam or effervescence
03	200	100 – test 2	No foam or effervescence
04	200	100 – test 2	No foam or effervescence

FIGURE III
DETERMINING AUTOCLAVE OPTIMAL
OPERATION TIME- TEST 1

Parameters	Inlet	0 min.*	30 min.	60 min.	90 min.
Pressure. Kpa		950	1025	800	740
Temperature. C		160	160	160	160
Sample - % solids	25.4	26.1	25.9	27.2	28.3
Volume	2.45	0.11	0.12	0.12	0.12
Solid weight	900	39.8	43.1	46.8	49.7
Limestone addition (5%)	-				
Solution analysis					
Ca	0.12	1.04	0.97	0.84	0.35
Mg	3.79	5.59	6.89	6.89	7.31
Mn	0.68	0.68	0.64	0.64	0.63
Si	0.25	0.27	0.30	0.30	0.25
Zn	31.7	14.6	2.06	2.06	1.20
PH	4.00	5.40	5.95	5.95	6.40
Zinc precipitation (%)		53.9	86.2	93.5	96.4

* heating time = 43 min

FIGURE IV
LIMESTONE ADDITION TO INCREASE
ZINC PRECIPITATION EFFICIENCY

Parameters	Inlet	0 min.*	60 min.	90 min.	Discharge
Pressure. Kpa			1800		-
Temperature. C		200	200	200	-
Sample - % solids	25.0		27.2	28.3	29.5
Volume	2.45		0.12	0.12	1.61
Solid weight	2520.8		46.8	49.7	705.4
Limestone addition (in g)	22				
Solution analysis					
Ca	0.12		0.28	0.27	0.38
Mg	3.79		3.79	5.15	6.77
Mn	0.68		0.47	0.09	less 0.01
Si	0.25		-	-	-
Zn	31.7		0.49	0.16	less 0.02
Ph	4.00		-	6.95	7.96
Fluorides (mg/L)	3.2				5.0
Zinc precipitation (%)			98.5	99.5	more 99.9

FIGURE V**LEACHING TEST USING TEST 2 CAKE**

Number	Quantity of Acid Solution in ml	Quantity of Cake from Autoclave in g	Visual check of foam formation	TOC Content (mg/l)
01	800	142 - test 2	No foam formation or effervescence	<4

* TOC: Total Organic Carbon

FIGURE VI
FLOW CHART FOR CONTINUOUS TEST RUN FOR 60 HOURS
WITH SHIFT OPERATING DUTY

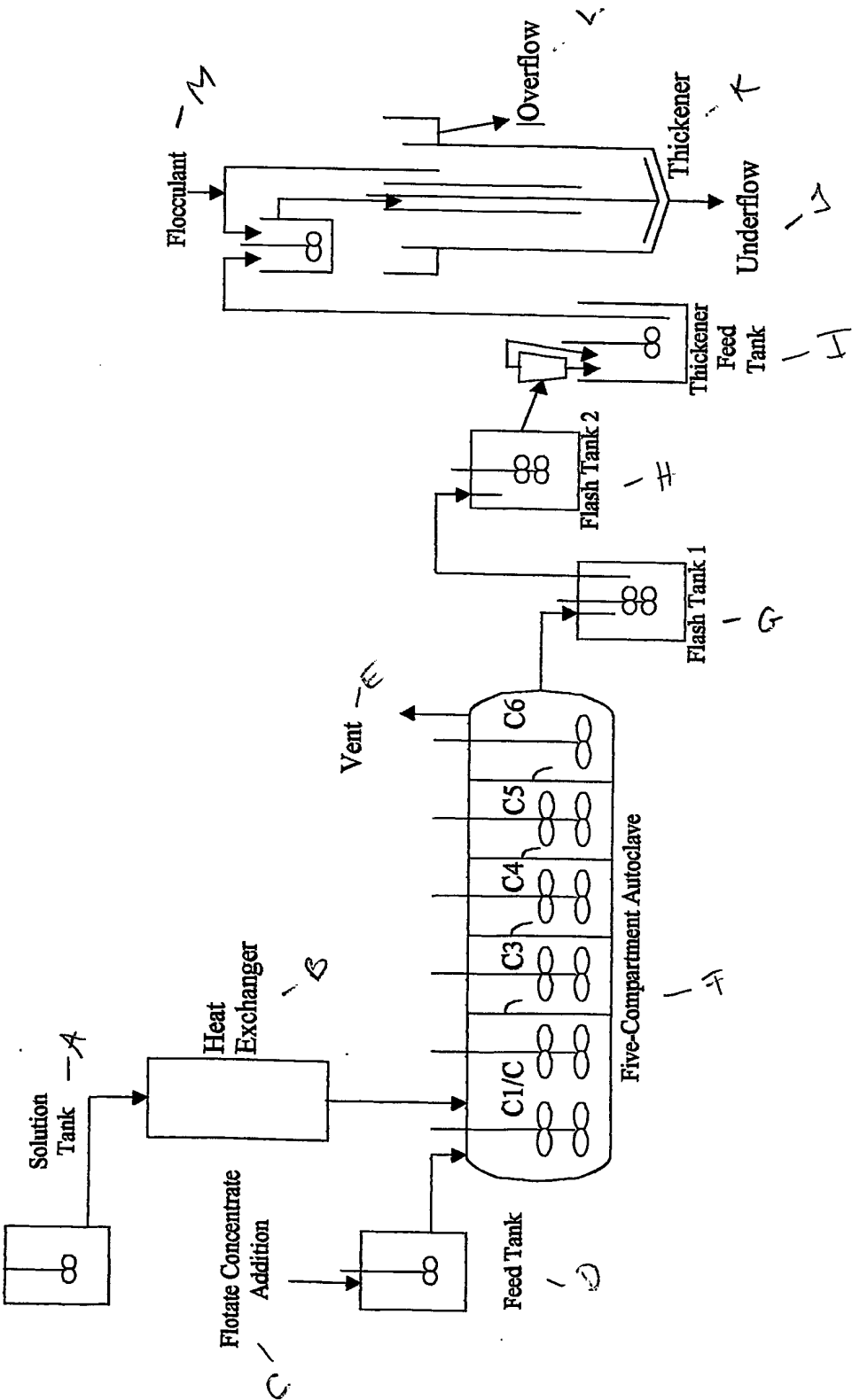


FIGURE VIII
RESULTS OF CONTINUOUS TESTS FOR AUTOCLAVE-TREATED FLOTATED CONCENTRATE

Solution analysis:

Date Shift	Jun 12 12 - 18	Jun 12 18 - 24	Jun 13 00 - 06	Jun 13 06 - 15	Jun 13 15 - 21	Jun 13 9 pm to Jun 14 3 am	Jun 14 03 - 08	Jun 14 08 - 12	Jun 17 07 - 17
Rotation Shift	6	12	18	27	33	39	44	48	58
Period	1	1	1	2	3	4	4	4	Demo
Solution Zinc	Secondary	35.2	35.2	35.2	35.2	35.2	35.2	35.2	35.2
	C1/C2	2.44	2.80	3.14	10.5	8.98	4.84	5.78	1.83
	C3	1.20	1.17	1.09	8.69	7.46	3.98	3.69	0.79
	C4	0.76	0.58	0.53	8.07	7.01	4.00	3.05	0.45
	C5	0.71	0.45	0.47	8.16	6.75	4.26	2.59	0.33
	C6	0.48	0.70	0.62	7.43	6.10	4.07	2.62	0.38
	Discharge Tank	0.17	0.17	0.13	4.29	3.34	3.30	0.70	0.04
pH	Thickener Overflow	--	0.22	0.15	--	3.51	3.53	--	0.62
	Secondary	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
	C1/C2	6.7	6.4	6.7	6.4	6.2	6.7	6.3	6.7
	C3	7.1	6.8	7.1	6.4	6.2	6.6	6.5	7.0
	C4	7.3	7.0	7.2	6.4	6.3	6.6	6.5	7.0
	C5	7.3	7.0	7.2	6.4	6.3	6.6	6.6	7.1
	C6	7.3	7.0	7.1	6.3	6.3	6.6	6.5	7.1
Zinc Precipitation Efficiency	Discharge tank	7.5	7.1	7.1	5.8	6.0	6.5	6.6	6.5
	Thickener Overflow	--	--	--	--	--	6.7	--	6.6
	C1/C2	92.1	91.0	89.9	67.2	72.0	84.4	81.4	94.1
	C3	96.1	96.2	96.5	72.8	76.7	87.1	88.1	97.5
	C4	97.5	98.1	98.3	74.8	78.1	87.1	90.2	98.5
	C5	97.7	98.5	98.5	74.5	78.9	86.2	91.7	98.9
	C6	98.4	97.7	98.0	76.8	81.0	86.9	91.6	98.8
Discharge Tank	Discharge Tank	99.5	99.5	99.6	87.5	90.3	90.1	97.9	99.9
	Thickener Overflow	--	99.3	99.6	--	89.8	89.4	--	98.1

FIGURE X
LEACHING OUTPUT OF AUTOCLAVE-TREATED FLOTATED CONCENTRATED

Concentrate	Period 1 – Jun 13	Period 4 – Jun 14
Zn %	43.61	44.25
SiO ₂ %	21.62	21.46
F %	236	236
Mg %	0.68	0.50

Residues	Period 1 – Jun 13	Period 4 – Jun 14
Zn %	1.81	1.84
SiO ₂ %	61.46	61.48
Output %	98.54	98.55

FIGURE XI**QUALITY OF THE SOLUTION RESULTING FROM LEACHING
COMPARED WITH THE CALCINE LEACHING PROCESS**

Primary Filtrate	Period 1 – Jun 13	Period 4 – Jun 14	Calcline
Zn g/l	134.8	133.7	133.2
H ⁺ g/l	38.2	38.7	39.2
Mg g/l	15.2	14.5	15.8
F mg/l	19.8	19.0	26.2
Co mg/l	4.74	4.52	4.74

FIGURE XII**TIME COMPARISON OF PERIOD 1 AND 4 FOR LEACH PULP FILTRATION VERSUS
CONVENTIONAL CALCINE PULP**

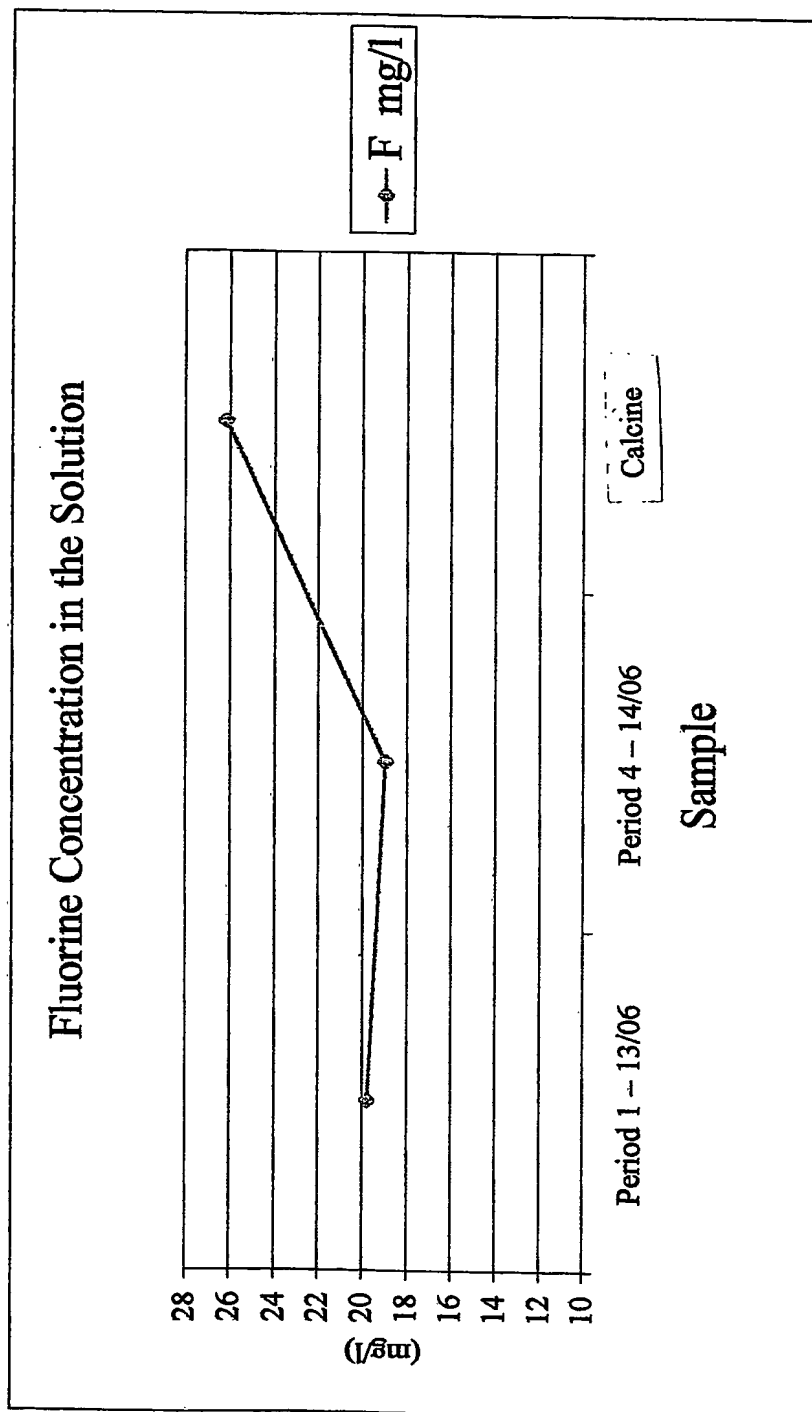
Pulp	Period 1 – Jun 13	Period 4 – Jun 14	Calcine
Time	3'12"	3'32"	5'26"

FIGURE XIII**COMPARATIVE SEDIMENTATION EFFICIENCIES
IN 250 ML TEST TUBE (33% DILUTION)**

Pulp	Period 1 – Jun 13	Period 4 – Jun 14	Calcine
1 minute	230	226	238
2 minutes	218	210	234
3 minutes	206	194	232
4 minutes	194	178	230
5 minutes	180	164	226

Therefore, the improved leaching sedimentation efficiencies were those in connection with the autoclave-treated floated concentrate

FIGURE XIV
SOLUTION FLUORIDE CONCENTRATION



The solution from the autoclave-treated leached silicate concentrate was 7 mg/l lower in fluorine concentration.

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/BR 03/00096

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C22B19/02 C22B19/20 C22B3/08 C22B3/20 C22B3/44

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C22B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 00 46412 A (COMPANHIA MINEIRA DE METAIS ;SOUZA ADELSON D (BR); MENDES MARCELO) 10 August 2000 (2000-08-10) page 3, line 12 - line 21	1-8
Y	EP 0 851 034 A (MITSUI MINING & SMELTING CO) 1 July 1998 (1998-07-01) page 2; figures 1,7	1-8
Y	DATABASE WPI Section Ch, Week 198917 Derwent Publications Ltd., London, GB; Class J01, AN 1989-127976 XP002259834 & R0 95 473 A (INTR METALELOR RARE), 30 September 1988 (1988-09-30) abstract	1,2,5,6
	-/--	

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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